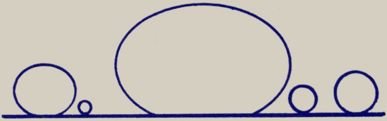
THINGS

of science



HYDROPHOBIC FUMED SILICA

Created and distributed without profit by Science Service, Inc., 1719 N Street, N.W., Washington, D. C. 20036. E. G. Sherburne, Jr., Director. Ruby Yoshioka, Editor.

HYDROPHOBIC FUMED SILICA

Hydrophobicity or water repellency is a very useful property. We are all familiar with its action, although we may not fully understand it. For example, it protects us from the wetness of the rain (water-repellent clothing); allows ducks to float on the surface of a pond (water-repellent feathers) and prevents plants from drowning in the dew condensing on their leaves (water-repellent leaves).

What makes a substance water repellent? An object may be hydrophobic due to its chemical nature or as a result of a combination of chemical and physical properties of its surface. But it can repel water only because of the behavior of water itself.

In this unit is a specimen of a highly water-repellent chemical, hydrophobic fumed silica. By doing the experiments you will understand why it is exceptionally hydrophobic and also learn about some of the interesting ways in which this characteristic can be applied.

First look over your materials.

HYDROPHOBIC FUMED SILICA—White powder in polyethylene bag; **do not** open the package until you have read the instructions given in the text.

ALUMINUM FOIL—Sheet of stiff aluminum foil; 3 x 5 inches.

SEEDS—Packet of zinnia seeds; variety Lilliput.

COLORED PAPERS—Two sheets; 3 x 5 inches.

The hydrophobic fumed silica was provided by the Cabot Corporation, Boston, Massachusetts, and is known under the trade name Silanox®.

HYDROPHOBICITY

All solid bodies keep their shape because they are held together by attractive forces between the molecules that compose them. The molecules of any particular substance are all alike and the greater the atttraction between them the more solid the object will be. This attractive force between like molecules is known as cohesion.

Liquids are also held together by cohesive forces, but not so strongly. The molecules in a liquid therefore can move about. This ability of the molecules to move freely gives liquids certain interesting surface characteristics. When a liquid is poured into a glass or jar, it assumes the shape of the container and the molecules within it are attracted with equal force on all sides. However, the molecules at the surface are attracted inward only, since there are no liquid molecules above them to exert an equal upward

pull. The greater downward attraction tends to pull the molecules at the surface into the liquid. As a result, the surface of the liquid tends to contract. The measure of this inward force on the surface molecules is referred to as the surface tension of the liquid. Surface tension varies from liquid to liquid.

The cohesive force between the molecules causes the surface layer to act like a thin elastic membrane. This characteristic of water is important in water repellency.

Experiment 1. Fill a bowl with water. Now place a paper clip on the end of a fork. Gently lower the fork into the water keeping the paper clip horizontal. Remove the fork carefully and slowly just as the paper clip touches the water's surface and it will remain afloat. If you look at the paper clip from an angle, you will see that the surface of the water is "stretched" downward like a membrane by its weight, but the force of the surface tension is great enough to support it.

Experiment 2. Place a drop of water on a piece of wax paper (or plastic wrapping). Note the shape of the surface of the drop not in contact with the paper. The molecules in a drop of a liquid are continually pulling the surface molecules toward the center and trying to occupy the smallest possible space. The geo-

metric shape that is most compact and has the least surface area is the sphere. Therefore, when no outside forces are acting upon a drop of liquid it will assume a spherical shape.

Experiment 3. Sprinkle a few drops of water on the outside of your THINGS of science box. Does the water cling to it and wet it? Molecules of water and other liquids are attracted not only to each other, but to molecules of other substances. Thus water may adhere to various materials. The attractive force between unlike molecules is called adhesion.

Now scatter several drops of water on the wax paper. Do they stick to the surface? Place the paper at an angle. Do the drops flow off?

When the cohesive force of the water molecules is greater than the adhesive force between the molecules of water and another substance, the water will not adhere to the surface. The surface tension of the water droplets form them into small spheres allowing them to roll off without wetting the surface. Such substances like the wax paper therefore repel water and are hydrophobic.

Place a drop of water on one of the sheets of paper in your unit. Notice how the drop clings to the paper and wets it. The attractive force of the paper for the water is greater than the cohesive force

within the water droplet, so the droplet becomes flattened and spreads increasing the area of contact with the paper. The paper is hydrophilic or water attracting rather than hydrophobic. If the paper is tilted the drop moves along leaving a wet trail.

Test various other materials such as cloth, metal and wood for hydrophobicity. Check the aluminum foil in your unit. Is it more or less hydrophobic than wax paper? Note the uses made of the various materials tested. Have any of them been treated to make them water repellent?

WHAT IS HYDROPHOBIC FUMED SILICA? (SILANOX)

Experiment 4. Lift the package of hydrophobic fumed silica powder and note how light it is. Observe how fine it is. The particles of fumed silica are submicroscopic in size.

When working with it handle the powder very gently and with a minimum of agitation since it floats readily in the air because of its fineness. Do not bring your face close to the powder or try to smell it. If it should scatter avoid breathing it in.

Gently cut a one-inch slit in one end of the package, just sufficient to allow a teaspoon to enter. This will help prevent

the powder from flying around.

Place a tiny bit between your fingers and feel it. It feels smooth and has a somewhat drying effect.

Be sure to wash your hands after experimenting with Silanox. Keep your hands away from your eyes. The powder may irritate them. Silanox is not toxic, but should be handled with respect just as you would any other chemical.

Experiment 5. Insert a teaspoon carefully into the slit in the bag and place some of the powder in a small shallow dish. Do not pour the powder from the spoon as you would sugar or salt. Transfer the powder to the dish by placing the spoon in the dish and then tilting it. Handle the powder in this way in all your experiments to minimize scattering.

Put a small drop of water from a spoon in the center of the powder. What happens? Does the powder absorb the water?

Tilt the dish slightly. What happens to the drop? Does it roll around like a marble? Notice how freely and effortlessly the drop moves over the surface of the powder.

Silanox is highly hydrophobic. Because of special characteristics it is much more hydrophobic than the wax paper or any of the other common water-repellent substances.

Cover the drop with some of the

powder. Does it roll around beneath the powder just as easily? Since hydrophobic fumed silica is extremely water repellent, the cohesive forces within the drop are not hindered by outside forces that may tend to weaken the surface tension and the surface can contract to the smallest possible size. Thus a small drop will form a perfect sphere and roll around virtually friction-free.

If a drop is large, however, gravity will tend to flatten it. Place a larger drop of water in the powder. Does it move around just as freely?

What makes this substance so highly hydrophobic?

Hydrophobic fumed silica is composed of a derivative of silicon. Silicon, the second most abundant element on earth, is found in nature as various oxides. One

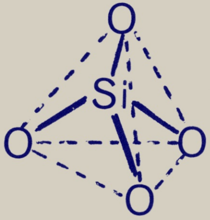


Fig. 1

of its most widely distributed forms is as silicon dioxide (SiO_2) or silica. In pure form silicon occurs as quartz and mixed with impurities it composes sand, sandstone, opal and other minerals.

In silica, the oxygen atoms arrange themselves around silicon in a three-dimensional tetrahedron (Fig. 1).

These oxides usually form chains in a lattice network bonded together tetrahedrally (Fig. 2).

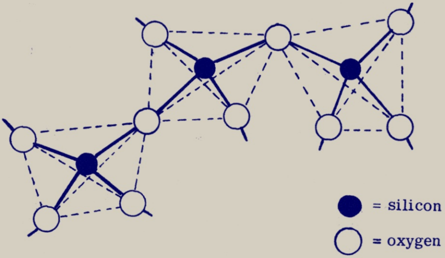


Fig. 2

Each tetrahedron thus is bonded to another tetrahedron of silicon and oxygen. The formula SiO_2, therefore, only represents the ratio of two oxygen atoms to each silicon atom.

Crystals of silicon dioxide are held together by extremely strong forces and

the bonds between the atoms are very difficult to sever. Such minerals as quartz and sand therefore are very hard and inert and because of the tetrahedral structure are jagged and have sharp points. It is because of this irregular pointed structure that sand serves so well as an abrasive.

Fumed silica is made by burning silicon tetrachloride at a high temperature in an oxygen-hydrogen flame. This process produces silica in the form of a very fine powder consisting of submicroscopic particles with a tremendous external surface area and a great quantity of surface atoms for reaction.

$$SiCl_4 + 2H_2O \xrightarrow{1100°C} SiO_2 + 4HCl$$

Surface atoms are those atoms that are not surrounded completely by other atoms and thus are free to react with other compounds. Many of the surface atoms of fumed silica have a hydrogen atom attached to the oxygen forming an —OH group (Fig. 3).

The OH group attached to the surface atoms causes fumed silica to be hydrophilic.

In order to produce hydrophobic fumed silica like the specimen in your unit, an organic group, trimethylsilyl, is

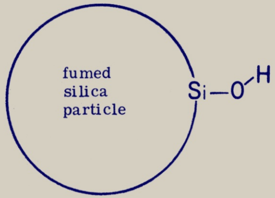


Fig. 3

substituted for the hydrogen atom by reaction first with a silane (Fig. 4).

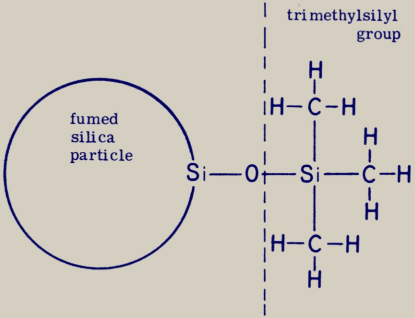


Fig. 4

The surface characteristic of silicon dioxide is changed by this reaction from hydrophilic to hydrophobic.

Surfaces such as the wax paper and polyethylene film are water repellent be-

cause of their chemical nature. In hydrophobic fumed silica, however, the water repellency results from both the chemical and physical properties of the substance.

A surface coated with Silanox becomes hydrophobic chemically because the organic surface groups (trimethylsilyl) repel water and physically because of the roughness imparted to the surface due to the layer of Silanox particles. Because of surface tension, the water droplets tend to rest on the points of the projections of the Silanox coating and do not penetrate into the valleys in between which are filled with air. This combined action of hydrophobicity and surface roughness produces a super-hydrophobic effect (Fig. 5).

Experiment 6. Cut your pink paper in half. Coat one half of the paper with the powder. To do this place a small amount (about 1/16 teaspoon) on the paper and rub it into it with the back of the bowl of a teaspoon. Take a small quantity of the substance at a time and rub it into the entire surface being sure to leave no section uncoated.

After you are sure the surface is completely covered, place a small drop of water on the center of the paper. Place a drop also in the center of the untreated half. Compare the reaction of the drops of water. On the untreated paper, the

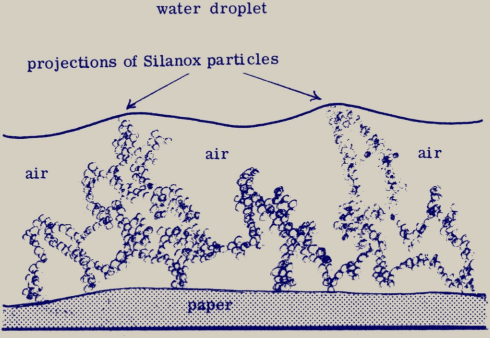


Fig. 5

adhesive forces dominate, while on the treated paper, the cohesive forces exceed the adhesive forces.

Notice how extremely water repellent the coated paper has become. Lift the paper slightly from one edge. Observe how quickly the water is shed. The compound thus can be used to protect the surfaces of paper, nonwoven fabrics, textiles, wood and other materials.

Experiment 7. Cut your piece of aluminum foil lengthwise into two strips 5 x 1½ inches in size. Coat one of the strips with the powder, rubbing it in with the back of the spoon as you did in coating the paper. Use small amounts of the

Silanox at a time. Treat both sides of the strip being sure to cover the entire surface.

Now place the coated and uncoated aluminum strips side by side on a horizontal surface and place a drop of water on the center of each strip.

Look at the shape of the drops from the side and note any differences. Is one more spherical than the other? If so, which? Aluminum foil is hydrophobic, but its water repellency can be greatly increased by coating it with Silanox.

The degree of hydrophobicity can be measured by observing the contact angle of the drop. The contact angle is the angle that a water droplet forms with the surface upon which it rests. The larger the contact angle, the greater the degree of water repellency (Fig. 6).

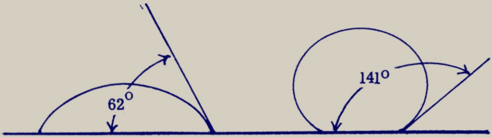


Fig. 6

The contact angle of water on most surfaces, even those which are nonwettable, rarely is greater than 110°, while that of water on surfaces coated with

Silanox are generally between 125° to 150°.

Which of the drops on the aluminum sheets has the greater contact angle? The more spherical the drop, the greater its contact angle.

Experiment 8. Place several drops of water on the treated aluminum foil. Note how quickly it rolls across the surface.

Now fill a glass with water. Insert the treated aluminum strip vertically into the water. Observe the surface of the water next to the aluminum strip and also along the sides of the glass.

Note that the water at the sides of the glass rises up a little forming a concave

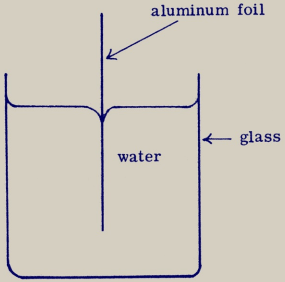


Fig. 7

surface upward. This is because water adheres to glass.

What is the shape of the surface of the water next to the aluminum strip? Can you explain your observation? (Fig. 7).

Repeat the experiment with the untreated aluminum foil. What do you find?

Experiment 9. Now take the coated aluminum strip and lightly push it at an angle against the surface of the water. What happens? It is repelled and does not penetrate the surface.

Repeat using the uncoated aluminum strip. Notice how easily it enters the water.

Experiment 10. Fill a bowl with water and place the coated aluminum strip in it. Does it float? Push it down into the water. Does it rise again to the surface? Its hydrophobicity prevents it from sinking. The tiny pockets of air also add to its buoyancy.

Repeat the experiment with the untreated aluminum. Does it sink to the bottom?

Experiment 11. Take your strip of paper that has been coated on one side with the powder. Place it vertically into a glass of water as you did the aluminum foil. Look through the glass at the coated side. Does it have a silvery sheen?

Look at the uncoated side. Note that no sheen is present.

The silvery sheen is caused by the air layer entrapped between the paper and the water. The hydrophobicity of the chemical and the air layer prevent the water from reaching the surface of the paper. Remove the paper and note that although the untreated side is wet, the coated surface has remained dry.

The behavior of the powder duplicates a natural phenomenon known as the gaseous plastron effect possessed by some aquatic insects. These insects have tiny hydrophobic fibrils on their bodies which allow the formation of an air layer. When the insects go underwater, they are able to breathe because of this air layer.

The next time you have an opportunity to observe an uderwater insect, look for the silvery sheen of the gaseous plastron.

Hydrophobic fumed silica simulates another natural phenomenon. A dewdrop on a leaf may assume an almost spherical shape just as a tiny droplet of water does on a Silanox-coated paper or aluminum. The dewdrop rests on the tiny hydrophobic fibrils present on the leaf, but does not penetrate between the fibrils allowing transpiration to continue.

Experiment 12. Mix two teaspoons of Silanox with 4 teaspoons of rubbing alcohol (isopropyl alcohol), until it completely disperses.

Cut a six-inch square piece from an old

nylon hose. Spread it out and hold it under a tap. Note that water passes right through it.

Now place the nylon piece in the alcohol-powder mixture and wet it thoroughly with the solution, being sure no dry spots remain. Spread it out and hang it by one edge allowing it to drip dry overnight.

When it is thoroughly dry, place it under a tap and allow water to flow into it. What happens? The water remains on the nylon. Allow about a tablespoon of water to remain on the nylon and bring up the sides to form a bag. The water remains encased in the nylon.

The openings in the nylon mesh are not actually sealed by a solid film of the chemical, but the water is prevented from escaping by surface tension and by the pockets of air formed between the water and the particles.

Now wet your finger and touch the outside of the nylon bag. Does a stream of water flow out from the particular spot you touched and only from that spot? By placing your wet finger against the nylon, you have destroyed the surface film of the water at that point since water adheres to water. The water thus was able to penetrate the air pocket and an opening through which the water could escape was created.

Empty the nylon bag of all the water

and note that it is perfectly dry.

Refill it. You will find that the opening you had made is no longer there and the water remains in the bag.

Splash water against the nylon mesh and note how readily it sheds any water that comes in contact with it.

Silanox thus provides water repellency to a cloth without sealing it. The cloth remains breathable.

Treat other pieces of cloth with the powder and make them water repellent. When applied to outdoor textiles such as tent and awning canvas, it protects the cloth from wetting-out and resulting leakage.

If you have some gauze, coat it also. Does it become water repellent? Bandaging treated with the material provides resistance to external water staining while still retaining the breathability essential for healing.

Experiment 13. Cut a 1 x 3-inch strip from the yellow sheet of paper in your unit and coat both sides thoroughly. Place it in one of the compartments of an ice tray. In another compartment place an untreated strip of the same size. Fill the tray with water. After the water has frozen, remove the pieces of paper from the ice. Note that the ice is readily released by the treated paper while it sticks to the uncoated strip.

If Silanox is coated on ship rigging and other surfaces where ice buildup is severe, the ice could be readily released or even prevented from forming.

Another use for the compound is in concrete forms. Since concrete is a water system, if the form is coated with Silanox, the low degree of adhesion would provide easy release after cure.

Experiment 14. Take a teaspoon of the flour and place it in a small dish or custard cup. Note that the flour particles tend to stick together.

Now take a half a teaspoon of the hydrophobic fumed silica and mix it with the flour thoroughly. Does the flour become free flowing?

Small quantities of the chemical impart hygroscopic powders with flowability. In powders which attract water, the particles of Silanox act like tiny "ball bearings" allowing the powder particles to roll past one another easily.

The compound may be used in such powders as fire retardants and fertilizers which have a tendency to cake in damp weather.

Experiment 15. Mix one teaspoon of the powder with one-half teaspoon of salad oil. Does it absorb the oil? Stir the mixture and it will form a smooth gel.

Hydrophobic fumed silica repels water

but attracts oil. Thus it is also oleophilic.

This property has various useful applications, such as in the cleaning up of oil spills.

Experiment 16. Take the remaining yellow paper and coat it on both sides with the powder.

Cut it into strips about one-half-inch wide.

Fill a shallow bowl with water and place a drop of oil, such as salad oil in the water.

Lay the pieces of coated paper on the drop of oil. Note that they absorb the oil while repelling the water. After they become saturated with oil, the pieces of paper do not sink but remain afloat maintaining their water repellency.

In the cleaning of oil spills at sea, it is important to remove the oil as rapidly as possible to prevent evironmental damage. By treating the surface of the absorption agents such as straw, waste paper and wood waste with hydrophobic fumed silica only the oil would be absorbed by these materials. After absorbing the oil, they could be easily removed since they will remain on the surface. In untreated form, the absorption agents soon become water-soaked and sink below the surface interfering with oil absorption. Since the treated materials attract only the oil, their efficiency is increased.

Experiment 17. Place about two inches of water in a large mayonnaise jar or similar container. Add to this about one tablespoon of the powder. Then cover the jar tightly and shake it vigorously. Some of the particles will become emulsified in the water while the rest will remain at the surface forming a layer.

Allow the particles to settle before removing the lid. Look to see that the surface of the water is completely covered by the powder. It should be about ⅛-inch thick.

Now sprinkle some of your zinnia seeds over the surface. Cover the jar loosely and place it in a warm dark place.

After about two days, examine the seeds to see if any have germinated. Some of the seeds may already have long roots. Examine them again after another day or two. Do you see the first leaves?

If you wish, you can add some plant food to the water. The seedlings will remain afloat supported by the powder and continue to grow. The tiny plants can be easily removed without damage to the roots and may be transplanted to a pot or other prepared bed if desired.

Silanox serves as an excellent germinating medium because of its low release of water and its high air content. With just enough water and plenty of aeration, seeds will germinate quickly.

Transplant the seedlings outdoors only after the last frost. Plant them about six inches apart and one-eighth inch deep in prepared soil. The Lilliput zinnia will grow to a height of about two feet.

Experiment 18. Think of other ways in which hydrophobic fumed silica may be used and devise experiments to test your ideas.

Appreciation is expressed to the Cabot Corporation for their cooperation in preparing this unit.

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